



## **Soil organo-mineral associations fine structure: nanoscale TEM-EELS imaging of Fe Si Al-organic matter coprecipitates**

Nithavong Cam (1), Clément Levard (1), Jérôme Rose (1), Emmanuel Doelsch (2), Bertrand Devouard (1), and Isabelle Basile-Doelsch (1)

(1) Aix Marseille Univ, CNRS, IRD, INRA, Coll France, CEREGE, Aix-en-Provence, France, (2) CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France

Organo-mineral interactions are recognized as a key factor in stabilizing organic matter (OM) in soils and short-range order mineral phases are increasingly considered as key mineral phases in the control of OM dynamics (Rasmussen et al., 2018). Coprecipitation is the main mechanisms involved (Chen et al., 2014; Mikutta et al., 2014). A recent conceptual model proposes that coprecipitates form continuously upon soil mineral weathering in contact with organic compounds of the soil solution (Basile-Doelsch et al., 2015). For silicate minerals, this process implies that Si may also take part in the structure of coprecipitates. However, only Fe and Al coprecipitates have been considered as coprecipitating cations in the literature.

Nanophases were precipitated from a solution containing ionic Fe, Al, Si, Mg and K, obtained from a biotite weathered leachate. TEM and Fe K-edge EXAFS showed that they were structured mainly by small oligomers of Fe, together with Si and Al (Tamrat et al., 2018). By adding an organic ligand (DOPA, initial M:C $\approx$ 1), coprecipitates were structured by a loose and irregular 3D network of small oligomers of Fe, Si and Al forming a highly reactive open-structured mineral skeleton on which OM was bond. A conceptual 3D model of these “nanoCLICs” (Nanosized Coprecipitates of inorganic oLIgomers with organiCs) has been proposed (Tamrat et al., submitted). It differs significantly from the previous models presented for Ferrihydrite and amorphous Al(OH)<sub>3</sub> coprecipitates (Kleber et al., 2015).

The present work seeks to validate this model using TEM imaging method, whose spatial resolution is adapted to the heterogeneity observed at the nanometer scale. The EELS elemental mapping revealed that the coprecipitates were composed of a mix of Fe Al Si and C down to the nanometer scale. No pure zone of Fe or C were observed, but Fe rich and C rich areas could be detected. The M/C ratio varied from 0.5 to 1 between areas spaced of a few nanometers only. These observations are concordant with OM bonds to small oligomers of Fe, Si and Al, as described in the nanoCLICs model. This work also shows that the high spatial resolution and the diversity of analyzed elements by TEM-EELS make this technique an excellent choice for the characterization of soil organo-mineral associations.

Basile-Doelsch, I., Balesdent, J., Rose, J., 2015. Environ. Sci. Technol. 49, 3997–3998.

Chen, C., Dynes, J.J., Wang, J., Sparks, D.L., 2014. Environ. Sci. Technol. 48, 13751–13759.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., Nico, P.S., 2015. Chapter One, in: Sparks, D.L. (Ed.), Advances in Agronomy. Academic Press, pp. 1–140.

Mikutta, R., Lorenz, D., Guggenberger, G., Haumaier, L., Freund, A., 2014. Geochim. Cosmochim. Acta 144, 258–276.

Rasmussen, C., Heckman, K., Wieder, W.R., Keiluweit, M., Lawrence, C.R., Berhe, A.A., Blankinship, J.C., Crow, S.E., Druhan, J.L., Hicks Pries, C.E., Marin-Spiotta, E., Plante, A.F., Schädel, C., Schimel, J.P., Sierra, C.A., Thompson, A., Wagai, R., 2018. Biogeochemistry 137, 297–306.

Tamrat, W.Z., Rose, J., Grauby, O., Doelsch, E., Levard, C., Chaurand, P., Basile-Doelsch, I., 2018. Geochim. Cosmochim. Acta 229, 53–64.